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Development of Hydrogen Production Catalysts from Dimethyl Ether

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Abstract

Dimethyl ether (DME) is expected as one of clean fuels. We have been studying on DME steam reforming for hydrogen production. Copper alumina catalysts prepared by the sol-gel method produced large quantities of H_2 with DME steam reforming. Aiming at practical use of the catalysts, some experiments were carried out such as catalyst life time tests (durability test) and fixation of the catalysts on commercial catalysts in order to reduce the pressure loss and in order to make the catalysts inexpensive. In the case of the 240-h accelerated durability test, there is no deactivation, so that the sol-gel Cu-Zn/Al_2O_3 catalysts have long durability. The catalysts are easy to fix on the spherical aluminas, and the fixing (coating) makes less the amount of the sol-gel catalysts in the whole catalysts including the alumina. In case of coated spherical alumina (1-2 mm diameter) catalyst, the amount of the sol-gel Cu-Zn/Al_2O_3 catalyst was cut down into 1/5 times comparing with the sol-gel powder catalyst. This fixation on commercial spherical alumina will make the price of the catalyst inexpensive, and the pressure loss will be able to decrease. The further development is still need, but the catalysts have enough capability for practical use.

1 Introduction

It is expected that fuel cell is one of the methods for restraint of the global green effect. Steam reforming of fossil fuels is actively researched and developed as hydrogen supply methods for the fuel cells. Dimethyl ether (DME) does not contain the poisonous substances, and it burns without particulate matters (PM), without sulfur oxide (SOx), and with less nitrogen oxide (NOx). DME is expected as a clean fuel for the 21st century [1, 2]. DME has also recently become a potential fuel for hydrogen production to be used in fuel cells. DME is able to take the place of light oil and liquefied petroleum gas (LPG), and its physical properties are similar to those of LPG. There is possibility that DME infrastructures will be settled more rapidly than those of hydrogen, because LPG infrastructures existing are able to be used for DME.

I have been studying on steam reforming of DME for the hydrogen production. The new type catalysts prepared by a sol-gel method have been developed [3-5]. These catalysts produce hydrogen more effectively at lower reaction temperature than mixed catalysts with DME hydrolysis catalysts and methanol steam reforming catalysts. Cu-Zn (29-1wt. %)/Al_2O_3 is the most effective catalyst for hydrogen production in my recent study.

Aiming at practical use of the catalysts, catalyst life time tests (durability tests) were carried out. In order to reduce the pressure loss and in order to make the catalysts inexpensive,

fixation of the catalysts on commercial aluminas was examined. In this paper, the details are commentated.

2 Experimental

Cu-Zn(29-1wt.%)/Al_2O_3 powder catalyst prepared by the sol-gel method [3-5] was used for this study. The preparation method is mentioned in previous papers, and some catalysts were ground by an agate mortar to less than 150 μm diameters [3-5]. The other catalysts were fixed on commercial spherical aluminas (KHO-12S (diameter 1-2 mm) and KHO-24S (diameter 2-4 mm) manufactured by Sumitomo Chemical Co., Ltd.). The spherical aluminas were immersed in the sol condition precursor of the sol-gel Cu-Zn/ Al_2O_3 catalyst. The immersed catalysts were dried using a rotary evaporator. The dried catalyst was calcined at 500 ^oC for 5 h and was reduced by flowing H_2 at 450 ^oC for 10 h. This severe pretreatment was particularly performed for reactive comparison to avoid the catalytic deterioration with sintering of the catalyst by the reaction heat on continuous experiments with the same catalyst. For the durability test, the catalyst reduced at 350 ^oC for 5 h. Usually DME steam reforming is carried out under atmospheric pressure, but reaction pressure was 0.3 MPa for the accelerated durability test. Therefore, atmospheric pressure and pressurized reactors were used for the DME steam reforming, respectively. The supply of the reaction gas to the catalyst layer was adjusted to several space velocity by the flow speed and concentration of reactant (Ar with DME/steam = 1/3), except of DME/steam = 1/4 for the durability test. The reaction gas and products were analyzed by gas chromatographs (TCD, FID, and methanizer). The atmospheric pressure reactor was part of a closed circulation system. Before the reaction, the BET specific surface area of the catalyst in the reactor without the exposure to the air was measured using N_2 gas at −196 ^oC. After the evacuation of N_2 gas at room temperature for 30 min, the amount of CO it adsorbed in the same reactor without the exposure of the air was analyzed using CO gas at 0 ^oC. After the evacuation of CO gas at 300 ^oC for 1 h, steam reforming of DME over the same catalyst was performed in the same reactor without the exposure of the air.

The surface of the spherical alumina catalyst coated by the sol-gel Cu-Zn/Al_2O_3 catalysts prepared by the sol-gel was analyzed using a scanning electro-microscope (SEM, KEYENCE VE-9800).

3 Results and Discussion

3.1 Observation of catalysts

The photos of the catalysts prepared by the sol-gel method are shown in Figure 1. Figure 1(a) is the photo of the powder catalysts prepared by the sol-gel method. Usually Cu-Zn/ Al_2O_3 catalysts prepared by the sol-gel method were ground to less than 150 μm diameters, and these catalysts were used in the previous research [3-5]. Figure 1(b) is the SEM photo of the developed catalyst for this study on this paper. The sol-gel Cu-Zn/ Al_2O_3 catalyst was coated on the spherical alumina by immersing in the sol condition precursor of the sol-gel Cu-Zn/ Al_2O_3 catalysts. For practical use, pressure loss should be reduced. Therefore, spherical aluminas (KHO-12S & KHO-24S) were used as the supports of the catalysts. Figure 1(b) shows the catalysts that spherical alumina (KHO-12, 1-2 mm diameter)

was coated with the sol-gel Cu-Zn/ Al_2O_3 catalyst, and the sol-gel Cu-Zn/ Al_2O_3 catalyst looks well coated on the spherical alumina.

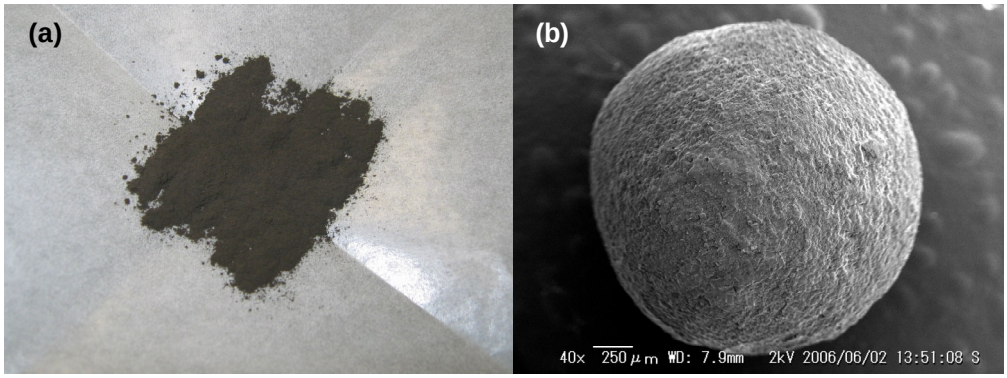

Figure 1: Photos of used catalysts in this research.
(a) Powder catalysts (sol-gel Cu-Zn/Al_2O_3, diameter < 150 μm) after the calcinations
(b) SEM photo of the spherical alumina (1-2 mm diameter) coated Cu-Zn/Al_2O_3 (sol-gel) catalyst

3.2 Physical properties of these catalysts

Coating percent was estimated from the increased amount of the catalysts by the fixation of sol-gel Cu-Zn/ Al_2O_3 catalyst. As shown in Table 1, KHO-12S (1-2 mm diameters) was coated in higher amount of 5.96 % than that of KHO-24S (3.56 %). Values of the BET specific surface area were decreased with the increase of the percent of sol-gel Cu-Zn/ Al_2O_3 catalyst coating. Amount of CO adsorbed is related to amount of active sites, dispersion of metal, and so on. Amounts of CO adsorbed were increased with the increase of the coating percent of sol-gel catalyst.

Table 1: Physical data of the Cu-Zn/Al_2O_3 powder catalyst and the coated catalysts on the spherical aluminas.

Catalyst	Coating percent (%)	BET surface area ($m^3\ g^{-1}$)	CO adsorbed ($\mu mol\ g^{-1}$)
Cu-Zn/Al_2O_3 (Powder)	-	215	20
Cu-Zn/Al_2O_3/spherical Al_2O_3 (KHO-24S, 2-4 mm)	3.56	200	46
Cu-Zn/Al_2O_3/spherical Al_2O_3 (KHO-12S, 1-2 mm)	5.96	160	76

3.3 DME Steam reforming over these catalysts

The three catalysts were used for DME steam reforming. The used each catalyst whole weight (including spherical alumina and coated sol-gel Cu-Zn/ Al_2O_3 catalyst), sol-gel Cu-Zn/ Al_2O_3 catalyst weight, and DME conversion over each catalyst are shown in Table 2. Main

products were H_2 and CO_2. The catalyst whole weight was increased for high conversion as shown in Table 2. The DME conversion of the sol-gel Cu-Zn/ Al_2O_3 powder catalyst and Cu-Zn/ Al_2O_3/spherical Al_2O_3 (KHO-24S) was around 95 %, even if the reforming temperature was 275 ^oC. Cu-Zn/ Al_2O_3/spherical Al_2O_3 (KHO-12S) should have been slightly more weight for around 95 % DME conversion at 275 ^oC of the reaction temperature. However, the DME conversion of the all catalysts at 300 ^oC was almost 100 %, respectively. Therefore, the fixation of sol-gel catalyst on commercial spherical alumina made the weight of the sol-gel Cu-Zn/ Al_2O_3 catalyst reduced. In case of coated spherical alumina (1-2 mm diameter) catalyst, the amount of the sol-gel Cu-Zn/ Al_2O_3 catalyst was cut down into 1/5 times comparing with the sol-gel powder catalyst. This fixation on commercial spherical alumina will make the price of the catalyst inexpensive, and the pressure loss will be able to decrease.

Table 2: Comparison of DME conversion over the Cu-Zn/Al_2O_3 catalyst and the Cu-Zn/Al_2O_3 coated spherical alumina catalysts.

Catalyst	Weight of catalyst (g)	Weight of sol-gel catalyst (g)	DME conversion at 275 ^oC (%)	DME conversion at 300 ^oC (%)
Cu-Zn/Al_2O_3 (Powder)	0.10	0.10	95	100
Cu-Zn/Al_2O_3 /spherical Al_2O_3 (KHO-24S, 2-4 mm)	1.42	0.050	99	100
Cu-Zn/Al_2O_3 /spherical Al_2O_3 (KHO-12S, 1-2 mm)	0.30	0.018	87	98

3.4 Accelerated durability test of the DME steam reforming catalysts

Usually DME steam reforming is carried out under atmospheric pressure, but as the accelerated durability test the reaction pressure was 0.3 MPa and the reaction temperature was 320 ^oC. The Cu-Zn/ Al_2O_3 powder catalyst and the Cu-Zn/ Al_2O_3 coated KHO-12S alumina catalyst were used for this test. The part of the results on the Cu-Zn/ Al_2O_3 (sol-gel) powder catalyst is shown in Figure 2. There was no big deactivation. Cu-Zn/ Al_2O_3 (sol-gel) is sufficiently durable catalyst. This catalyst will be used in practical. However, in case of the Cu-Zn/ Al_2O_3 (sol-gel) coated alumina catalyst DME conversion and the activity slightly decreased. After this durability test, the sol-gel catalyst was peeled off from the spherical alumina. In this time, the fixed catalyst was made by soaking the alumina into the sol condition of Cu-Zn/ Al_2O_3. It was suggested that the improvement of the fixation method is necessary.

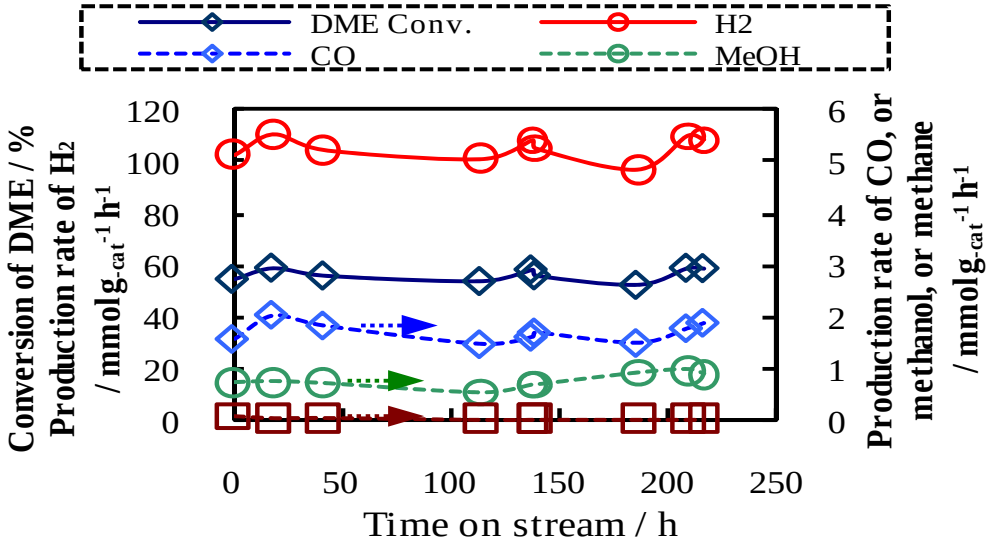

Figure 2: **Time course of DME conversion and production rates on DME steam reforming at 320 °C and under 0.3 MPa over Cu-Zn/Al_2O_3 powder catalyst prepared by the sol-gel method. Reaction temp.: 320 °C, reaction material SV: 2.0x103 h-1, DME/H_2O = 1.0/4.0.**

4 Conclusion

The sol-gel Cu-Zn/ Al_2O_3 catalysts have long durability, and the catalysts are easy to fix on the spherical aluminas. The further development is still needed, but the catalysts have enough capability for practical use.

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